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THE EFFECTS OF α -CARBORANE ON THE STRUCTURAL MORPHOLOGY OF SEGMENTED POLYURETHANE ELASTOMERS

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Introduction

Segmented polyurethane elastomers are a versatile and therefore highly commercially important class of physical elastomer. The unique combination of desirable mechanical, optical, structural and chemical properties^{1,2,3} found in PU elastomers, is a consequence of the microphase-separated structure of these materials⁴. However, with the ever increasing demand for improved, better defined, tunable or even novel physical and chemical properties in polymeric materials - researchers are looking towards new methods of property modification and control in polyurethanes and related systems.

One area of research that is receiving much attention is so-called 'nano-modification' of polymeric systems^{5,6} which is to say; the incorporation of a nanoscale secondary or tertiary phase into a polymeric system either through physical blending or chemical hybridization. One such class of 'nanoscale' material that has been the focus of recent interest as a property modifier in polymeric materials, are *carboranes*. These boron containing compounds, generally expressed by the molecular formula $C_2B_nH_{n+2}$, exhibit many desirable properties, in particular, high thermal stability and chemical stability, and show unusual chemistry not encountered in other materials.⁷

In this work, icosahedral *ortho*-carborane cages have been covalently incorporated into the hard segment of a methylenediisocyanate-polytetramethylene glycol (MDI-PDMG PU) segmented polyurethane elastomer and a combination of solid state NMR and thermal analysis techniques have been employed to characterize the effects of carborane cage inclusion on the morphology and dynamics of the polyurethane system.

Experimental

Materials. 4,4'-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) were obtained from Sigma Aldrich. Poly(tetramethylene glycol) (Terathane®) with molecular weights of ~1, 1.4 and 2 KDa were obtained from Invista and 1,2-dihydroxymethyl- α -carborane (CBD) was obtained from Dr. Mark Lee at the University of Missouri-Columbia.

Synthesis of polyurethane/carborane hybrid elastomers. Polyurethane/carborane elastomer systems were prepared incorporating 0-21.2% mass fraction carborane diol as a substitute chain extender, 1,4-butanediol and a polyol segment of 1.4 KDa) to yield a matrix of 8 systems. The elastomers were prepared by a two-step or quasi pre-polymer method in the following manner: PTMEG was pre-dried under vacuum at 100°C for a minimum of 2 hours. Excess MDI was charged into a 100 ml three-necked round bottom flask equipped with a mechanical stirrer and nitrogen inlet and melted at 75°C. The melted PTMEG was added to the melted MDI and the solution allowed to stir for 2 hours at 75°C to form a quasi pre-polymer. Carborane diol was added to the solution and allowed to stir for 1 hour at 75°C to begin chain extension. The temperature was raised to 100°C for an additional hour. The quasi prepolymer was cooled to 40°C and the appropriate amount of 1,4-butanediol was added to complete chain extension. The samples were hand mixed for 90 seconds, degassed, poured into molds (2.25"x2.25"x0.125"), and cured at 110°C for 16 hours. The cured elastomers were removed from the molds and placed in convection oven at 110°C for 8 hours and then post-cured at 80°C for 24 hours. The baseline polyurethane elastomers have a 50% of soft segment concentration (elastic %) with subsequent reactions keeping MDI and PTMEG amounts constant and the amount of BDO and CBD varied during chain extension.

Instrumentation. Low field solid-state NMR studies were performed on a Bruker Minispec spectrometer at 37±0.1°C under *static* conditions. Ninety degree pulse lengths of $\tau_p = 2.25 \mu s$ and recycle delays of 15 seconds were used. A solid echo 2D experiment was performed (see Figure 1).

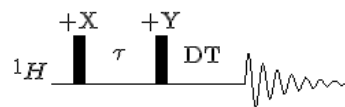


Figure 1. Proton 2D solid echo pulse sequence. (the interpulse delay time, tau was varied from 0.017 to 0.2 μs)

The 2D data set was fit to **Eqn. 1:**

Where T_{ei} is the decay constant for the decay of the solid echo for region i , T_{2i} is the typical T_2 for region i , δ is the pulse duration, τ is the interpulse delay, and $S_i(0,0)$ is the intrinsic signal due to region i . It is the intrinsic signal that represents the relative abundance of the domain in the 2-phase PU system comprised of rigid 'hard-segments' and soft-segments. Therefore the relative fraction of rigid domain observed can be given by **Eqn. 2:**

All pyrolysis studies were carried out using a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 GC using an Agilent 5973N quadrupole MSD for detection of analytes. Samples (~0.05 mg) of each hybrid elastomer were pyrolysed at a heating rate of 100 °C/min, from 60 to 1000 °C under a purge flow of helium. A 1:20 split flow from the pyrolysis chamber was injected continually into the GC HP-5 analytical column under constant flow conditions of 1 ml/min Helium as the carrier. The GC oven was set hold isothermally at 300 °C for a total run time of 15 minutes. The thermal degradation of each system was therefore characterized by collecting total ion chromatogram (TIC) master curves in each case, representative of degradation as a function of temperature and volatile products evolved.

Differential scanning calorimetry was carried out using a TA instruments Q1000 DSC in a modulated mode. 6 mg samples of each elastomer were prepared in pinhole hermetic pans and ran under a 20 ml/min purge flow of nitrogen from 0 to 250 °C at a rate of 5 °C/min (modulated).

Results and Discussion

Pyrolytic analysis of PU/carborane hybrid elastomers. The thermal stability of the synthesized materials and their non-oxidative degradation chemistry was investigated by means of analytical pyrolysis. Shown in Figure 2 are the degradation thermograms of the base PU and hybrid systems.

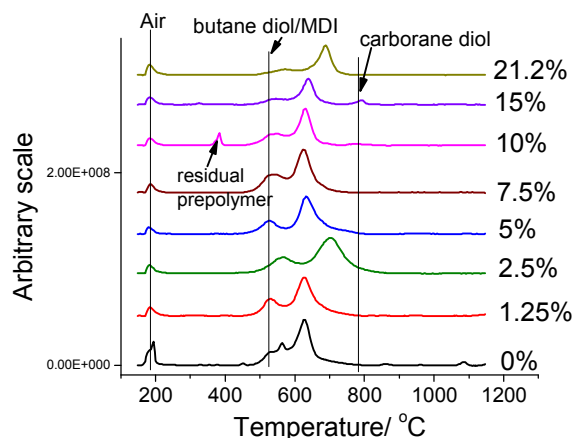


Figure 2. Degradation thermograms of the base PU and hybrid systems. The polyurethane degradation is typically observed as a two stage process which is altered significantly by the inclusion of carborane into the matrix

It can be observed from these pyrolysis data that as the level of carborane is increased, the degradation of the PU systems is shifted to higher temperatures and the low temperature loss of depolymerized butane diol is

exchanged for a much higher temperature loss of carborane diol. The relative levels of volatile material evolved on degradation decrease by ~60% between the base material and the 21.2% carborane system – overall these data indicate that there is a significant alteration in the condensed phase degradation behavior of the PU on the addition of carborane.

DSC analysis. DSC was employed to assess the effects of carborane inclusion on the crystalline morphology of the segmented elastomer. Shown in Figure 3 are the composite DSC thermograms for the synthesized systems.

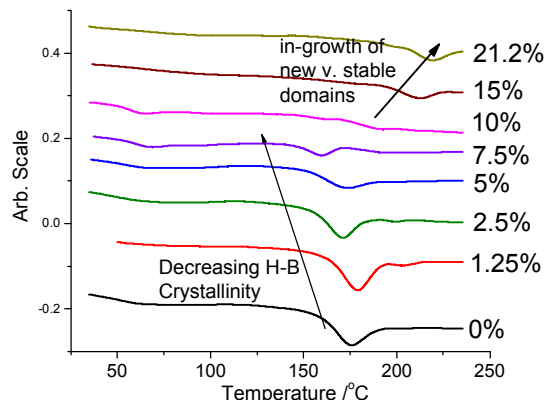


Figure 3. Composite DSC thermograms for the PU-carborane systems showing a progressive decrease in hard-block crystallinity with increasing carborane content coupled with the ingrowth of a new high temperature domain at loadings above 10 wt. %.

From the DSC analysis of the crystalline morphology of the systems it can clearly be observed that as the levels of carborane are increased, there is a distinct loss of hard block crystallinity, dropping from 14 to ~0% between the base and 10 wt. % carborane systems. These data appear to show that the inclusion of the carborane cage in the hard segments disrupts the ability of the segment to crystallize, effectively homogenizing the material to form a more disordered and homogeneous system. Interestingly, there is evidence that at loadings above 10 wt. % carborane, a new high temperature crystalline domain may be present – recent spin diffusion and microscopy studies (not included here) suggest that the domain sizes of this phase are on the a nano-scale.

Solid state NMR analysis. The effects of carborane inclusion on the morphology of the PU system have been investigated further by means of 2D solid echo NMR. While DSC provides a direct measure of only the crystallinity of the systems, these NMR experiments can provide an assessment of the relative fractions of mobile vs. rigid material as a whole. This rather broadens the definition of the effective ‘hard-segment’ to mean the rigid fraction of the system as a combination of both crystalline and constrained ‘interphase’. Shown in Figure 4 is the percentage observed fast relaxing, ‘rigid’ component of the PU systems as a function of carborane loading.

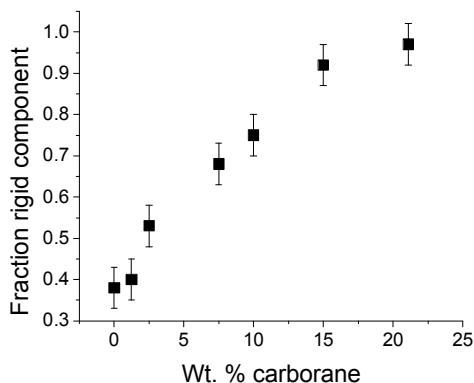


Figure 4. NMR derived ‘rigid’ fraction as a function of increasing carborane inclusion level.

From the NMR analysis it can be observed that as the carborane content is increased, the fraction of material in the system observed to be fast relaxing and therefore effectively ‘rigid’, increases from ~40% in the base system (a level comparable with the synthetic strategy) to 98% in the 21.2 wt. % carborane-PU hybrid. From the DSC data there were strong indications that the systems become more amorphous with increasing carborane content and the NMR analysis supports this assertion. It appears clear that by including carborane in the PU as a substitute chain extender, the order of the crystalline, phase separated hard-block is destroyed and a more amorphous and homogeneous structure is formed which is likely to be akin to semi-rigid interphase.

Conclusions. Carborane diol has successfully been incorporated into a MDI-BDO-PTMG segmented polyurethane elastomer as a substitute chain extender at a mol. ratio of 0-1%. The resultant materials show significantly altered high temperature thermal degradation and condensed melt phase behavior. These alterations in thermal properties are linked to observed changes in the structural morphology of the PU-carborane hybrids, which are less crystalline and significantly less phase separated than the base PU. The morphological properties are likely to be due to the presence of the carborane cage in the hard-block forming region of the ter-polymer, the sterics of which inhibit the development of long range crystalline order of the MDI residues.

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